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Reaction of Chloramines, Part IV¹⁾

The Reaction of Chloramines with β -Ketoesters and β -Diketones[†]

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The reaction of chloramines with β -ketoesters and β -diketones have been shown to yield the two corresponding fragmentation products, amides and dichloroderivatives. The results of this study indicates that the reaction is initiated by the addition of chlorinium cation to the enolic C=C double bond, and subsequent decomposition occurs via dichloroketoester or diketone as transient intermediates. The behavior of the C-C bond fission is characteristic of the varieties of chloramine.

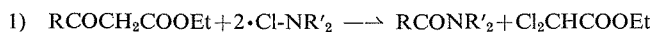
INTRODUCTION

In the previous communication,²⁾ the authors reported that β -diketones, when reacted with chloramines, decomposed with ease to the mixture of amide and dichloroketone. Based on the products, it has been proposed that the reaction proceeds through a cyclic six-membered transition state. The present paper deals with the products and mechanism of the reaction of β -ketoesters and several other β -diketones with chloramines.

RESULTS

1) The reaction of chloramines with β -ketoesters. Ethyl acetoacetate and ethyl benzoylacetate as substrate were allowed to react with chloramine in ether solution.

Table 1. Reaction of β -Ketoesters with Chloramine



	Ketoester	Chloramine	Amide	Yield %	Dichloroester	Yield %
1	$\text{CH}_3\text{COCH}_2\text{COOEt}$	NH_2Cl	CH_3CONH_2	55 ¹⁾	$\text{Cl}_2\text{CHCOOEt}$	+
2	$\text{C}_6\text{H}_5\text{COCH}_2\text{COOEt}$	NH_2Cl	$\text{C}_6\text{H}_5\text{CONH}_2$	72	$\text{Cl}_2\text{CHCOOEt}$	+
3	$\text{CH}_3\text{COCH}_2\text{COOEt}$	$(\text{CH}_3)_2\text{NCl}$	$\text{CH}_3\text{CON}(\text{CH}_3)_2$	96	$\text{Cl}_2\text{CHCOOEt}$	95
4	$\text{C}_6\text{H}_5\text{COCH}_2\text{COOEt}$	$(\text{CH}_3)_2\text{NCl}$	$\text{C}_6\text{H}_5\text{CON}(\text{CH}_3)_2$	97	$\text{Cl}_2\text{CHCOOEt}$	88
5	$\text{CH}_3\text{COCH}_2\text{COOEt}$	$(\text{C}_2\text{H}_5)_2\text{NCl}$	$\text{CH}_3\text{CON}(\text{C}_2\text{H}_5)_2$	97	$\text{Cl}_2\text{CHCOOEt}$	93
6	$\text{CH}_3\text{COCH}_2\text{COOEt}^{2)}$	ONCl	$\text{CH}_3\text{CON}\bigcirc$	89	$\text{Cl}_2\text{CHCOOEt}$	+

1) $\text{CH}_3\text{COCCL}_2\text{COOEt}$, 37%

2) in CH_3CN , Dioxane

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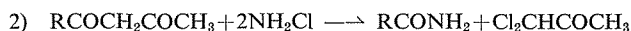
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The results of the reaction are presented in Table 1.

In all of the reaction (entries 1-6), two fragmentation products, amide and dichloroester, were isolated from the reaction mixture, and dialkylamides and dichloroester in these products were identified by their GLC retention times and by their IR-spectra. When ethyl acetoacetate was treated with chloramine, ethyl α,α -dichloroacetoacetate was obtained in 37% yield, and it was also the case by 8 hrs' heating of the reaction mixture. However, this fact strongly suggested that the reaction proceeded through this dichloroketoester as intermediate. The decomposition of ketoester with N-chloropiperidine in ether (entry, 6) resulted in a poor yield, but the use of acetonitrile or dioxane as solvent rendered the subsequent cleavage facile to give a satisfactory yield of the corresponding fragments.

2) The reaction of chloramine with β -diketones. Acetylacetone, benzoylacetone, *p*-methylbenzoylacetone, *p*-bromobenzoylacetone and dimedone listed in Table 2 were subjected to this series of experiment.

Table 2. Reaction of β -Diketones with Chloramine.



	R	Yield %	m.p.
7	CH ₃ -	87	81°
8	C ₆ H ₅ -	72	130°
9	<i>p</i> -CH ₃ C ₆ H ₄ -	52	157-158°
10	<i>p</i> -BrC ₆ H ₄ -	94	189-190°
11	Dimedone	99*	159°

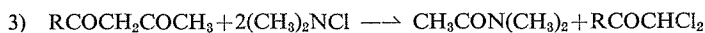
* 2-Chlorodimedone

A prolonged heating as long as 12 hrs was required for the reaction to complete, but all the possible products, which could result from the fission of a C-C bond, were formed in analogy with β -ketoester. On the other hand, a cyclic 1,3-diketone, dimedone with chloramine (entry, 11) gave rise to only 2-chlorodimedone and the cleavage of the carbocyclic ring was not observed at all.

3) The reaction of N,N-dimethylchloramine with β -diketone. With dialkylchloramine, β -diketones underwent a reaction similar to that observed with chloramine. The results were summarized in Table 3.

However, when benzoylacetone, *p*-methyl-, *p*-methoxy- and *p*-bromobenzoylacetone were treated with dimethylchloramine, an anomaly came out; instead of the

Table 3. Reaction of β -Diketones with N,N-Dimethylchloramine.



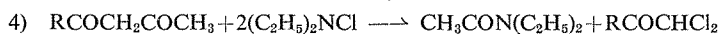
	R	Amide	Yield %	Dichloroketone	Yield %
12	CH ₃ -	CH ₃ CON(CH ₃) ₂	96	—	
13	C ₆ H ₅ -	CH ₃ CON(CH ₃) ₂	95	C ₆ H ₅ COCHCl ₂	72
14	<i>p</i> -CH ₃ C ₆ H ₄ -	CH ₃ CON(CH ₃) ₂	89	<i>p</i> -CH ₃ C ₆ H ₄ COCHCl ₂	82
15	<i>p</i> -CH ₃ OC ₆ H ₄ -	CH ₃ CON(CH ₃) ₂	85	<i>p</i> -CH ₃ OC ₆ H ₄ COCHCl ₂	69
16	<i>p</i> -BrC ₆ H ₄ -	CH ₃ CON(CH ₃) ₂	68	(<i>p</i> -BrC ₆ H ₄ COCHCl ₂)	—
17	<i>p</i> -NO ₂ C ₆ H ₄ -	<i>p</i> -NO ₂ C ₆ H ₄ CON(CH ₃) ₂	22	CH ₃ COCHCl ₂	+

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expected products, N,N-dimethylacetamide and the derivatives of phenacylidenechlorides, which could possibly result from the reversal regiochemistry, were isolated in good yield. The experimental data (entries, 13, 14, 15 and 16) demonstrate that such is the case with these substrates. The products were characterized by n.m.r. and other physical data. In contrast, the reaction of *p*-nitrobenzoylacetone with dimethylchloramine (entry, 17) afforded the fragments, *p*-nitrodimethylbenzamide and dichloroacetone in poor yield, where the decomposition occurred in the same manner with use of chloramine. Mechanistic argument of this peculiar behavior will be made later in some detail.

4) The reaction of β -diketones with N,N-diethylchloramine (entries, 18, 19 and 20) resulted in the same as that of dimethylchloramine shown in Table IV.

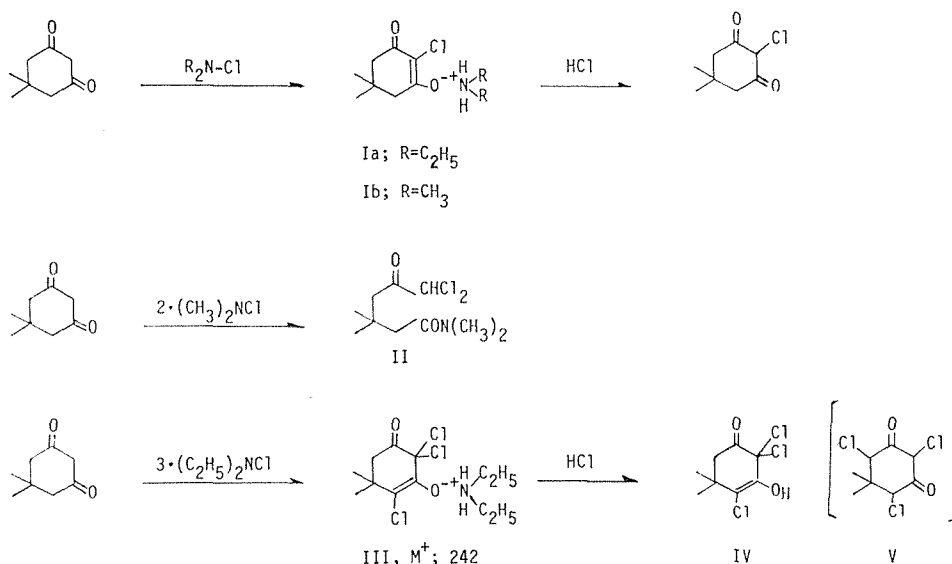
Table 4. Reaction of β -Diketones with N,N-Diethylchloramine.



	R	Amide	Yield %	Ketone	Yield %
18	CH ₃ -	CH ₃ CON(C ₂ H ₅) ₂	92	—	—
19	C ₆ H ₅ -	CH ₃ CON(C ₂ H ₅) ₂	93	C ₆ H ₅ COCHCl ₂	71
		C ₆ H ₅ CON(C ₂ H ₅) ₂	trace	CH ₃ COCHCl ₂	+
20	<i>p</i> -BrC ₆ H ₄ -	CH ₃ CON(C ₂ H ₅) ₂	72	(<i>p</i> -BrC ₆ H ₄ COCHCl ₂)	—

5) The reaction of dialkylchloramines with dimedone (Scheme 1). As previously described, the reaction of dimedone with chloramine gave 2-chlorodimedone, whereas the reaction of dimedone with one mole of N,N-diethylchloramine and N,N-dimethylchloramine afforded the stable adducts (Ia and Ib). The structure assigned to Ia and Ib was consistent with analyses and n.m.r. data. Mass spectral data of Ia indicated

Scheme 1



the molecular ion peak at m/e 174, which was identified as that of the chlorodimedone. Actually, Ia was hydrolyzed to this chlorodimedone with acid. Adduct Ib also underwent similar hydrolysis to give the same compound.

The ring fission product, an oily substance II was obtained by treating dimedone with 2 moles of dimethylchloramine along with aliphatic diketones. (Assignment of the structure is based on the n.m.r. spectrum.) Moreover, dimedone reacted with 3 moles of diethylchloramine to yield an adduct (III) containing three chlorine atoms. Mass spectrum of this adduct revealed the typical pattern owing to three chlorine atoms and molecular ion peak at 242 corresponding to the tri-chlorodimedone. In practice, III was converted by the acid hydrolysis into tri-chlorodimedone, whose analytical value was in good agreement with that of the theory. This fact suggested that the product should be either IV or V of the possible structural isomers, but the structure V was excluded on the ground of the melting point in the literature³⁾ (m.p. 89°C) and the alternative structure IV was preferred. The n.m.r. spectrum also afforded the corroborating suggestion for IV.

DISCUSSION

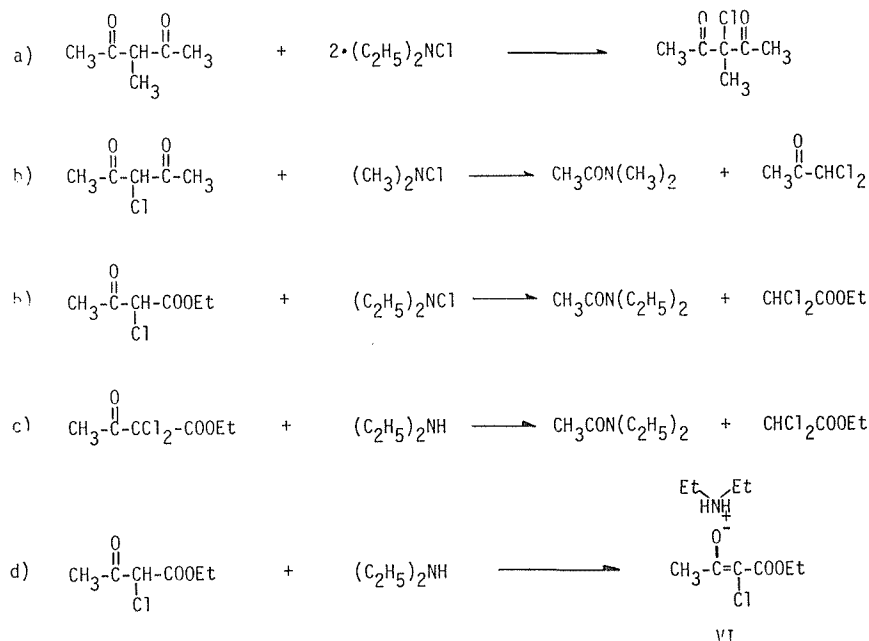
It has previously been shown that β -diketones cleaved to give a mixture of amide and dichloroketone, and based on the products, a cyclic transition state was proposed for the reaction. The results obtained in the present study suggested that the C-C bond fission proceeds by a mechanism different from that reported in earlier investigation.²⁾

The mechanism of the C-C fission must take into account two essential observations, i) that the interrupt of the reaction at an initial stage gave ethyl α -chloroacetoacetate in a detectable amount (characterized by glc and n.m.r. spectrum), ii) the primary reaction proceeds via intermediary ethyl α,α -dichloroacetoacetate, which could be isolated in a satisfactory amount. iii) On the other hand, it is known⁴⁾ in particular that such dichloro-compounds are hydrolyzed by treatment with amines under mild condition to give the similar fragmentation products in analogous to the basic cleavage of β -diketone itself. On the basis of these facts, it is thus reasonable to presume that the reaction proceeds successively through monochloro- and dichloro-ketoesters as intermediate, followed by the addition of amines to decompose into two fragments.

In order to justify the validity of such an assumption, the following reactions were designed (Scheme 2). a) Should the C-C fission occur through dichloro-compound, one might expect that the such a cleavage would not be realized with the α -monoalkyl substituted compound. Actually, α -methylacetylacetone reacted with 2 moles of N,N-dimethylchloramine only to give the corresponding monochlorodiketone and the cleavage was not observed at all. b) The reaction of monochlorodiketone and ketoester with one mole of dialkylchloramine readily gave the corresponding amides and dichlorides, accompanied by the fission of C-C bond. c) The C-C bond of dichloroacetoacetate was cleaved by the treatment with diethylamine into the same fragments under quite the same condition, just as did the original ketoester with diethylchloramine.

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Scheme 2



d) Under the same condition, monochloroester did not undergo the cleavage, but an unstable adduct VI was isolated in a nearly quantitative yield. Its n.m.r. spectrum was characteristic of the proposed structure, showing two triplets at 1.2 ppm ($J=7$ Hz, 6H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$) and at 1.3 ppm ($J=7$ Hz, 3H, $-\text{COOCH}_2\text{CH}_3$), apparent quartet at 2.8 ppm ($J=7$ Hz, 4H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$) and 4.25 ppm ($J=7$ Hz, 2H, $-\text{COOCH}_2\text{CH}_3$), a singlet at 2.35 ppm (3H, $-\text{COCH}_3$) and a very broad singlet due to two hydrogen atoms on ammonium ion centered at 6.5 ppm.

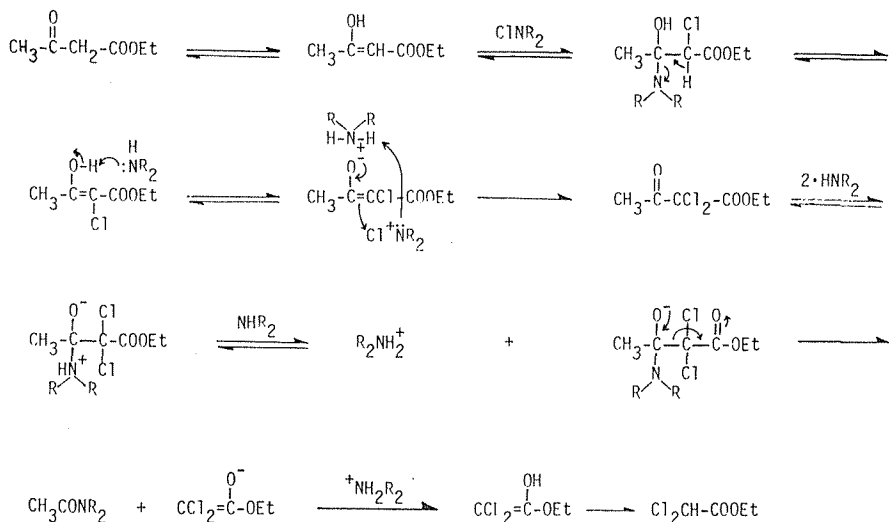
In view of these data as described above, the following mechanism can be proposed to account for this anomalous behavior (Scheme 3.). Namely, the reaction was initiated by the attack of Cl^+ to the enolic $\text{C}=\text{C}$ double bond and gave first α -monochloroacetate. And next, it can be assumed that the amine present free in solution attached to the ester so as to form the adduct, such as actually observed to be the case in the experiment d. Furthermore, this adduct underwent a reaction with another mole of chloramine to afford the intermediary of dichloroketoester in the fashion of reaction as indicated by arrow. Finally, the cleavage of the carbon-carbon bond was envisioned as the addition of the amine to the dichloroester and subsequent decomposition of this intermediate into the two carbonyl fragments, similar to that observed for the basic hydrolysis of *N*-methyl anilides⁵⁾ and benzoic anhydride.⁶⁾ This is also the case for the β -diketones.

A different situation prevails in the reaction of β -diketones with chloramines:

$$\begin{array}{c}
 \text{O} \quad \quad \text{O} \\
 \parallel \quad \quad \parallel \\
 \text{R}-\text{C}-\text{CH}_2-\text{C}-\text{R}'
 \end{array}$$

For the unsymmetrical β -diketone, $\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_2-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}'$, two mode of cleavage, leading to two different fragments were found (Tables 3 and 4 as compared with Table 2 with

Scheme 3



use of chloramine as such). It is thought that this causes the reversal of regioselectivity of amine to the intermediary of dichlorodiketone. The factors governing the direction of amine are still obscure, but it seems to be possible to interrupt the behavior at the dichlorodiketone stage as given below. If this phenomenon were due solely to electronic effect, one may well account for all of the results in Tables 3 and 4. That is, a nucleophilic dialkylamine HNR_2 will most likely attack the more electrophilic carbonyl groups. Thus the amide RCONR_2 should be formed in preference to $\text{R}'\text{CONR}_2$, if R is a stronger electron attractor than R' . Accordingly, it was considered that in *p*-nitrobenzoylacetone, where the nitro group withdraws electron by its resonance effect through the conjugated system, HNR_2 attacked at the acyl carbon atom adjacent to *p*-nitrophenyl group, resulting in the formation of *p*-nitrobenzamide and unsym-dichloroacetone. While in benzoylacetone, *p*-methyl-, *p*-methoxy-, and *p*-bromo-benzoylacetone as such, supplying the electron to conjugate systems, the attack of amine takes place on an acyl carbon atom not adjacent to such groups, thus the cleavage of these compounds yielded mainly acetamide and the corresponding phenacylidene-chlorides. However, this argument cannot explain the reason, why a different manner of cleavage is possible in the reaction of chloramine, giving rise to the benzamides rather than acetamide (Table 2).

Therefore, we will now apply the knowledge of the substitution reaction of ambident nucleophiles in order to explain this specific mode of attack of chloramines. If the nucleophilicity of NH_3 is stronger than NHR_2 , it appears that NH_3 tends to attack the less electrophilic carbon with the character of $\text{S}_{\text{N}}1$ reaction, whereas NHR_2 attacks the more electrophilic carbonyl group with the character of a bimolecular substitution. Since NH_3 easily attacks the acyl carbon of dichloroester adjacent to the electron-supplying phenyl groups, and benzamides and dichloroacetone are formed actually. On the other hand, dialkylamine attacks the more electrophilic acyl carbon

to yield the reverse fragmentation products. Such a hypothesis makes it possible to interpret the reaction mechanism to some extent. However, it is also anticipated that this addition process may probably be a reflection of complex results caused by both the electronic and steric effects of alkyl substituents on nitrogen atom. We will follow up further this observation by a series of experiments.

EXPERIMENTAL

Materials. The commercial ethyl acetoacetate, ethyl benzoylacetate, acetylacetone, benzoylacetone and dimedone were used for the experiment without further purification. The following β -diketones were prepared by methods described in the literature; *p*-Methyl-, *p*-methoxy-, and *p*-nitrobenzoylacetone,⁷⁾ *p*-bromobenzoylacetone,⁸⁾ ethyl α -chloroacetoacetate and ethyl α,α -dichloroacetoacetate,⁹⁾ ethyl α -methylacetoacetate,¹⁰⁾ α -chloroacetylacetone.¹¹⁾

Reagents. Solutions of chloramines were prepared according to Coleman's procedure.¹²⁾ N-Chloropiperidine was prepared as described by Bock *et. al.*¹³⁾

General procedure. To the solution of substrate (0.045 mole) in 25 ml of dry ether was added the ethereal solution of chloramine (0.09 mole) all at once. The reaction mixture was stirred for 2 hrs under cooling in an ice bath, and stirring was continued overnight at room temperature. After the duration, it was heated under reflux with stirring until the reaction was completed. After the removal of solvent, the products were isolated. This was repeated in the same way or with a slight modification, with variations of other substrate. Unsubstituted amides immediately separated out in crystalline precipitate. N,N-Dialkylamides and phenacylidenechlorides were isolated by the fractional distillation in vacuo.

Identification of products. Identification of the reaction products was obtained by gas-liquid chromatography (Shimazu Model-3AH with a 3 m \times 3 mm column of DEGS, 20% on Neosorb; column bath temp. at 150°C; carrier gas H₂ 40 ml/min.), and by IR (Hitachi EP-S2), NMR (Varian A-60) spectra and elemental analyses (Yanagimoto CHN-corder TM-1). Melting points were uncorrected.

Acetamide (m.p. 78°C) and *benzamide* (m.p. 128.5°C) were identified by comparing their infrared spectra with those of the authentic specimen.

N,N-Dimethyl-(BP₂₅ 74–5°C), *N,N*-diethylacetamide (BP₃₀ 90–91°C) and *N,N*-dimethylbenzamide (BP₁₅ 132–3°C) were also identified by glc and IR-comparison with those of authentic samples.

N-Piperidinoacetamide (BP₃₀ 125°C). Retention time on glc was the same as that of the authentic sample, which was derived from piperidine and acetic-anhydride.

Ethyl dichloroacetate (BP 157–8°C). Retention time on glc was the same as the authentic specimen. NMR* (CCl₄): δ 1.35 (t, 3, J=7Hz, -COOCH₂CH₃), 4.3 (q, 2, J=7Hz, -COOCH₂CH₃) and 5.95 (s, 1, -CHCl₂).

Ethyl α -chloroacetoacetate and *dichloroacetate*. The retention times on glc coincided

* Chemical shifts are reported in values relative to TMS as an internal standard, and the data are given in the order of multiplicity (s; singlet, d; doublet, t; triplet, q; quartet and m; unresolved multiplet), integration and assignment.

with those of the authentic samples, which were prepared from ethyl acetoacetate and sulfuric chloride.⁹⁾

Unsym-Dichloroacetone (BP 120°C) was converted into the corresponding semicarbazone, melted at 164°C. NMR of dichloroacetone (CCl₄); δ 2.42 (s, 3, CH₃CO-) and 5.7 (s, 1, Cl₂CH-).

p-Methylbenzamide. m.p. 155–6°C, from H₂O (Lit.¹⁴⁾ 155°C).

p-Bromobenzamide. m.p. 189–190°C, from H₂O (Lit.¹⁵⁾ 190°C).

2-Chlorodimedone. m.p. 159°C, from benzene. IR-Spectrum was the same as the authentic sample.¹⁾

N,N-Dimethyl-p-nitrobenzamide. m.p. 101–2°C, from alcohol. NMR (CDCl₃); δ 3.1 (broad s, 6, -N(CH₃)₂), and 7.6 and 8.3 (dd, 4, J=8.5Hz, aromatic protons).

Phenacylidenechloride.¹⁶⁾ BP₂₅ 142–3°C. NMR (CDCl₃); δ 6.68 (s, 1, Cl₂CH-), and 7.6 and 8.1 (m, 5, aromatic protons). Hydrolysis¹⁶⁾ with dilute hydrochloric acid gave mandelic acid (m.p. 115–6°C).

p-Methylphenacylidenechloride. BP₂₅ 142–3°C. NMR (CDCl₃); δ 2.45 (s, 3, -COCH₃), 6.68 (s, 1, -CHCl₂), and 7.3 and 8.0 (dd, 4, J=9.0Hz, aromatic protons).

p-Methoxyphenacylidenechloride.¹⁷⁾ BP₁ 115–6°C, m.p. 75–6°C (from alcohol). NMR (CDCl₃); δ 3.9 (s, 3, -OCH₃), 6.68 (s, 1, -CHCl₂), and 6.99 and 8.1 (dd, 4, J=9.0Hz, aromatic protons).

Adduct Ia. Yield 70%, m.p. 86–7°C. NMR (CDCl₃); δ 1.05 (s, 6, gem-CH₃), 1.38 (t, 6, J=7Hz, -N(CH₂CH₃)₂), 2.3 (s, 4, ring protons), 3.1 (q, 4, J=7Hz, -N(CH₂CH₃)₂) and 7.45 (very broad s, 2, -N⁺H₂). The mass spectrum showed the molecular ion peak at m/e 174, which was superimposable with that of authentic sample, 2-chlorodimedone.

Anal. Calcd. for C₁₂H₂₂ONCl: C, 58.17; H, 8.95; N, 5.65. Found: C, 58.07; H, 8.95; N, 5.65.

Adduct Ib. Yield 83%, m.p. 160–1°C. NMR (CDCl₃); δ 1.05 (s, 6, gem-CH₃), 2.28 (s, 4, ring protons), 2.72 (s, 6, -N(CH₃)₂) and 8.75 (broad s, -N⁺H₂).

Oily product II. Support for the proposed structure was supplied only by its NMR spectrum (CDCl₃); δ 1.3 (s, 6, gem-CH₃), 2.65 (s, 2, -CH₂CON(CH₃)₂), 3.12 (s, 2, -CH₂COCHCl₂), 3.2 and 3.3 (ss, 6, -N(CH₃)₂), and 6.32 (s, 1, -CHCl₂).

Adduct III. m.p. 124–5°C, Yield 74%. NMR(CDCl₃); δ 1.35 (s, 6, gem-CH₃), 1.43 (t, 6, J=7Hz, -N(CH₂CH₃)₂), 2.6 (broad s, 2, ring protons), 3.16 (q, 4, J=7Hz, -N(CH₂CH₃)₂) and 9 (very broad s, 2, -N⁺H₂).

Anal. Calcd. for C₁₂H₂₀O₂NCl₃: C, 45.27; H, 6.35; N, 4.35. Found: C, 45.52; H, 6.36; N, 4.42.

2,2,4-Trichlorodimedone (2,2,4-Trichloro-5,5-dimethylcyclohexane-1,3-dione) (IV). m.p. 156–9°C. The structure was established by its NMR-spectrum. NMR (CDCl₃); δ 1.35 (s, 6, gem-CH₃), 2.75 (broad s, 2, ring protons) and 5.18 (broad s, enolic -OH).

Anal. Calcd. for C₈H₉O₂Cl₃: C, 39.46; H, 3.73. Found: C, 39.70; H, 3.74.

α -Chloro- α -methylacetylacetone.¹⁸⁾ BP₄₅ 140–1°C. NMR (CDCl₃); δ 1.75 (s, 3, -ClCCH₃-) and 2.33 (s, 6, 2·(CH₃CO-)).

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